Thermodynamic Consequences of Dynamical Instabilities in Common Lattice Structures

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Metallic elements usually crystallize in one of the bcc, fcc or hcp lattice structures. It is often assumed that the other of these structures represent metastable phases of the considered element. However, it has recently been noted that very frequently those phases are dynamically unstable rather than metastable, i.e. some of their phonon frequencies are imaginary. Among the many examples are Mg (hcp; bcc), Cu (fcc; bcc), W (bcc; fcc) and Re (hcp; bcc). In the parentheses, the observed structure under ambient conditions is here followed by a dynamically unstable structure. Analogously, the NaCl-type lattice is unstable in III-V semiconductors which have a stable diamond-type lattice. The instabilities may be present for phonons in the long-wavelength limit (i.e. violation of stability criteria on the single crystal elastic constants), as well as for short-wavelength phonons. A lattice may go from a dynamically stable to an unstable form through variation in atomic composition, pressure or temperature. In a dynamically unstable lattice, the concept of a vibrational entropy has no meaning and hence, e.g., the Gibbs energy is not defined. The paper discusses the consequences of this fact for thermodynamic properties, for instance in W-Re alloys where one hits an instability on alloying from either end of the pure components.